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OPTICAL MULTILAYER

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OPTICAL MULTILAYER

FIELD OF THE INVENTION

The present invention relates to an optical multilayer comprising a polymeric substrate having a non-zero out-of plane birefringence and an amorphous polymeric overlayer having an out-of-plane birefringence of opposite sign to the substrate. The multilayer has an overall low out-of-plane phase retardation.

BACKGROUND OF THE INVENTION

Due to the low material cost and ease of processing, polymeric materials are widely used in opto-electronic components. An ongoing objective is to replace inorganic glasses that are known to be "fragile", "heavy" and "hard for machining". Polymeric materials, however, have optical characteristics that are process dependent, especially birefringence. All optical grade polymers are transparent and amorphous. When amorphous polymers are processed into a desirable shape, they are not optically isotropic, unlike the inorganic glasses. That is, the three indices of refraction, nx, ny and nz, are not equal. This is due to polymer-chain orientation that is unique to polymers. Thus, given a process condition, the observed optical anisotropy depends on the degree of polymer chain alignment. Polymer molecules have intrinsic birefringence Δn_{int} that is determined by factors, such as the polarizabilities of functional groups and their bond angles with respect to the polymer chain. The polymer products have extrinsic birefringence (in-plane or out-of-plane) that is different from the intrinsic birefringence and that is strongly process dependent. Depending on the application, the birefringence has to be controlled to meet the application requirement. In many cases, it is desirable to have substantially low birefringence or phase retardation in both the in-plane and out-of-plane directions.

In the optical disk application such as Compact Disk (CD) and Digital Video Disk (DVD), the substrate materials must satisfy conditions such as, 1) high transmission, 2) low humidity permeation, 3) dimensional stability and 4) low birefringence. Typically, the reading of optical disks involves the detection of

slight changes n the polarization state or a change in the intensity of the reflected light from a disk surface. Thus, the birefringence in the disk substrate will have detrimental effects on the readout, such as read-error or noise. Optical disk substrates are manufactured by injection molding of polymers. Polycarbonate (PC) has been widely used for substrates for CD and DVD. It has high transmission, high dimensional stability against heat and humidity, and high mechanical strength. PC, however, has relatively high intrinsic birefringence Δn_{int}. The process of injection molding generates alignment of polymer chains. Thus, a polymer with high intrinsic birefringence, such as PC, is prone to generate unacceptable levels of in-plane retardation R_{in} and out-of-plane retardation R_{th}. In order to prevent this problem, one typically adjusts the molding conditions, such as temperature and flow-rate. This optimization of process conditions has been successfully applied to significantly reduce the R_{in} through the reduction of Δn_{in}. In some cases, the in-plane birefringence Δn_{in} for normally incident light can be made as low as $1{\sim}3\times10^{-5}$. On the other hand, the out-of-plane birefringence Δn_{th} is typically negative and with the optimized molding process the value is $-6{\sim}-5\times10^{-4}$. Even though the value of Δn_{th} is small, the corresponding phase retardation for obliquely incident light is not negligible due to the substantial thickness of substrate, ~1mm. Thus, the light incident on the substrate at an oblique angle φ (measured from the substrate normal direction) will suffer a phase retardation that scales as φ^2 for small φ. In some cases, the total phase retardation, taking into account reflection, at $\varphi=30^{\circ}$ can reach as much as -150nm.

In typical Liquid Crystal Displays (LCDs), a liquid crystal cell is situated between a pair of polarizers. Incident light polarized by the polarizer passes through a liquid crystal cell and is affected by the molecular orientation of the liquid crystal, which can be altered by the application of a voltage across the cell. The altered light goes into the second polarizer. Typical polarizers used widely for liquid crystal displays (LCDs) have a structure such that absorptive polarizing layer (e.g., iodine dye absorbed Polyvinyl Alcohol (PVA) layer) is sandwiched between the triacetylcellulose (TAC) substrate. TAC is widely used for polarizer manufacturing partly because of its low Δn_{int}. For a typical un-

stretched TAC, the Δn_{in} is in the order of 5×10^{-5}. Thus TAC with 100μm thickness has R_{in} ~5nm. This amount of phase retardation is not significant and light linearly polarized by the PVA layer essentially remains linearly polarized going through the TAC layer. However, this is true only when light is normally incident to the plane of the polarizer. Most of the TAC substrates are known to have negative Δn_{th} of the order ~-5×10^{-4}. That would give R_{th} ~ -50nm. This out-of-plane phase retardation R_{th} is responsible for the change in the state of polarization for obliquely incident light. It is favorable to have finite negative Δn_{th} in TAC substrates for some modes of LCDs. This is because of the fact that the negative R_{th} can compensate positive R_{th} of the liquid crystal molecules that are aligned perpendicular to the liquid crystal cell plane. However, negative Δn_{th} of TAC has a detrimental effect in the LCD mode where the liquid crystal remains essentially parallel to the plane of the cell. This is the case for In-Plane-Switching LCDs, in which liquid crystal molecules rotate while remaining substantially parallel to the plane of the cell.

In a typical backlight LCD, the backlighting assembly contains several optical films that improve the light distribution and polarization before reaching the liquid crystal cell. This backlighting assembly **201** is illustrated in FIG. 2. Light exiting the backlight, **203**, first encounters optical films that improve light distribution in the display, such as, diffusing films, **205** and brightness enhancement films, **207**. Light is then incident on a reflective polarizer **209** that contains a substrate, **211**, and a polarizing layer, **213**, which transmits one polarization state and reflects the other polarization state. The next component in the optical path is the absorptive polarizer **215**, which contains a bottom substrate, **217**, an absorbing polarizing layer, **219**, and a top substrate, **221**. The transmission axis of the absorptive polarizer and that of the reflective polarizer are parallel. Ideally, the polarization state that is transmitted by the reflective polarizer **209** is the same polarization state transmitted by the absorbing polarizer **215**. The optical stack between the backlight **203** and the reflective polarizer **209** recycles the polarization state that is reflected. The polarized light incident on the absorption polarizer **215** must be substantially linearly polarized so that light is effectively transmitted and not absorbed. As stated earlier, typical absorption

polarizers contain TAC as a substrate **217**, **221** on either side of the absorbing polarizing layer **219**. Negative out-of-plane birefringence of TAC used as the bottom substrate **217** converts the linearly polarized light, incident on the absorption polarizer **215**, to elliptically polarized light. The polarizing layer **219** will then absorb a portion of the elliptically polarized light. Thus, decreasing the light through put of the display. To have the most light through put, the bottom substrate **217** between the reflective polarizer **209** and the absorptive polarizing layer **219** must have small Δn_{th} and R_{th}.

As mentioned before, careful adjustment of the process can significantly reduce the Δn_{in}, thus the R_{in} of the polymeric substrate. It is conceivable that additional optimization of the processing condition would further decrease the residual negative Δn_{th}. However, it increases the manufacturing cost. Alternative method is to form a multilayer. That is to dispose an overlayer with positive R_{th} on the polymeric substrate having negative R_{th}. This process provides an optical multilayer that has low R_{th} ($-30nm<R_{th}<30nm$) for wavelength λ in the range $400nm<\lambda<700nm$.

Several methods of generating a layer with non-zero Δn_{th} thus R_{th} have been known.

As is well known to those who are skilled in the art, liquid crystals that is uniformly aligned perpendicular to the substrate generate positive Δn_{th} if Δn_{int} of liquid crystal is positive. Polymerizable liquid crystal, such as the one disclosed in US 6,261,649 gives perpendicular alignment. However, liquid crystal compounds generally have a high cost and creating a uniform alignment of liquid crystals in large manufacturing scale is complicated and not trivial. In some cases, it requires photo-polymerization process in order to freeze the perpendicular alignment, adding extra process and cost.

Li et al. (Polymer, Vol. 37, Page 5321-5325, 1996) describe the process of generating the non-zero R_{th} by spin-coating polyamides on a transparent substrate. The random orientation of polyimide polymer chain is generated. The disclosed process is simple coating of polymers. However, the

resulting Δn_{th} and R_{th} are negative. Therefore, the method only enhances the negativity of the Δn_{th} of the polymer substrates described above.

With process optimizations, it is difficult to obtain a polymer substrate with sufficiently small R_{th}. Also, the prior art fails to provide a simple method to generate a polymer layer with positive Δn_{th}, thus making the manufacturing process for the polymeric multilayer with low R_{th} difficult. Therefore, it is a problem to be solved to provide a polymeric multilayer and a simple method of making it where the multilayer includes a polymer layer with positive Δn_{th} that can be disposed on polymeric substrate with negative R_{th} to form a multilayer having low R_{th}.

SUMMARY OF THE INVENTION

The invention provides an optical multilayer comprising a polymeric substrate having a non-zero out-of plane birefringence and an amorphous polymeric overlayer that comprises an amorphous polymer having a Tg value above 160°C and having the sign of its out-of-plane birefringence opposite to that of said polymeric substrate so as to provide a total out-of-plane phase retardation of said optical multilayer of between −30nm and 30nm for wavelengths of light between 400 and 700nm.

The invention thus provides a polymeric multilayer and a simple method of making it where the multilayer includes a polymer layer with positive Δn_{th} that can be disposed on polymeric substrate with negative R_{th} to form a multilayer having low R_{th}.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 is a view of a layer with thickness d and x-y-z coordinate system attached to the layer;

FIG. 2 is an elevation schematic of the typical LCD backlighting unit;

FIG. 3A, FIG. 3B and FIG. 3C are elevation schematics of the optical multilayer;

FIG. 4A and FIG. 4B are schematic views of perpendicular alignment of liquid crystals, and random in-plane orientation of amorphous polymer chain, respectively;

FIG.5A and FIG.5B are elevation schematics of polarizer with optical multilayer;

FIG.6 is an elevation schematic of the optical recording medium;

FIG. 7 is a graph showing the wavelength λ dependence of the out-of-plane phase retardation R_{th} of the exemplary multilayer according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

The following definitions apply to the description herein:

Order parameter, S refers to the degree of alignment of the polymer with respect to the reference direction. It is given by S= $\frac{3\langle\cos\theta^2-1\rangle}{2}$, where θ is an angle between the reference direction and the individual segment in the polymer chain. Brackets $\langle\ \rangle$ indicate the statistical average. S can take value from –0.5 to 1.0.

In-plane phase retardation, R_{in}, of a layer **101** shown in FIG. 1 is a quantity defined by (nx-ny)d, where nx and ny are indices of refraction in the direction of x and y. x is taken as a direction of maximum index of refraction in the x-y plane and y direction is perpendicular to it. x-y plane is parallel to the plane **103** of the layer. d is a thickness of the layer in z-direction. The quantity (nx-ny) is referred as in-plane birefringence, Δn_{in}. The value of Δn_{in} is given at wavelength λ= 550nm.

Out of-plane phase retardation, R_{th}, of a layer **101** shown in FIG. 1 is a quantity defined by [nz-(nx+ny)/2]d. nz is the index of refraction in z-direction. The quantity [nz-(nx+ny)/2] is referred as out-of-plane birefringence, Δn_{th}. If nz>(nx+ny)/2, Δn_{th} is positive, thus the corresponding R_{th} is also positive. If

$nz<(nx+ny)/2$, Δn_{th} is negative and R_{th} is also negative. The value of Δn_{th} is given at λ=550nm.

Intrinsic Birefringence Δn_{int} of polymer refers to the quantity defined by (ne-no), where ne, and no are extraordinary and ordinary index of the polymer, respectively. The actual birefringence (in-plane Δn_{in} or out-of-plane Δn_{th}) of polymer layer depends on the process of forming it, thus the order parameter, and the Δn_{int}.

Amorphous means a lack of long-range order. Thus an amorphous polymer does not show long-range order as measured by techniques such as X-ray diffraction.

Transmission is a quantity to measure the optical transmissivity. It is given by the percentile ratio of out coming light intensity I_{out} to input light intensity I_{in} as $I_{out}/I_{In}\times 100$.

Chromophore herein is defined as an atom or group of atoms that serve as a unit in light adsorption. (*Modern Molecular Photochemistry* Nicholas J. Turro Editor, Benjamin/Cummings Publishing Co., Menlo Park, CA (1978) Pg 77). A non-visible chromophore is one that has an absorption maximum outside the range of 400-700nm.

Reference will now be made to the drawings in which the various elements of the present invention will be given numerical designations and in which the invention will be discussed so as to enable one skilled in the art to make and use the invention. It is to be understood that elements not specifically shown or described may take various forms well known to those skilled in the art.

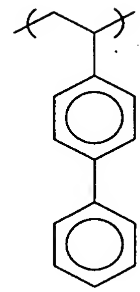
FIG.3A shows the structure of an optical multilayer **301** according to the invention. **303** is a polymeric substrate and **305** is an amorphous polymeric overlayer. The amorphous polymeric overlayer **305** can be disposed on both sides of the polymeric substrate **303** as shown in FIG. 3B. Two polymeric substrates **303** can be disposed on both side of the amorphous polymeric overlayer, FIG. 3C. The Δn_{th} of the polymeric substrate **303** is negative and that of amorphous polymeric overlayer **305** is positive. Generally, the value of Δn_{th} of the substrate **303** is extremely small ($-1\times10^{-4}\sim -3\times10^{-5}$). However, if the thickness of the

substrate **303** is significant (e.g. ~1mm), the R_{th} is not negligible and would be in the range of -100nm ~ -30nm. On the other hand, the Δn_{th} of the overlayer **305** is more positive than 5×10^{-3}(0.005). Thus, thickness of the overlayer **305** is much smaller than that of the substrate for an optical multilayer **301** with $-30nm<R_{th}<30nm$ for $400nm<\lambda<700nm$. For example, in order to balance the R_{th}= -50nm from the substrate **303** (e.g., thickness 1mm and Δn_{th}= -5×10^{-5}), the amorphous polymer overlayer **305** would only be 5μm, if Δn_{th} of the overlayer **305** is 0.01. To keep overall thickness of multilayer **301** within the reasonable range, the thickness of polymer overlayer **305** is preferably between 1 to 50μm or more preferably 5 to 20 μm. Transmission of the overlayer **305** should be high enough so that the overall transmission of the optical multilayer **301** remains high. The transmission of amorphous polymer overlayer **305** is preferably higher than 80% or more preferably higher than 90% for $400nm\leq\lambda\leq700nm$.

As is well known to those who are skilled in the art, the birefringence of amorphous polymer Δn_p is given by $\Delta n_p=S\Delta n_{int}$. In the prior art, a perpendicular alignment (in z direction in FIG. 4A) of liquid crystals **401** is used to generate positive Δn_{th}. In this case, S is in the range $0\leq S\leq 1$ and Δn_{int} is positive. If the polymer chain **403** is randomly oriented in the plane of the polymer layer as shown in FIG. 4B, the Δn_{th} is generated while Δn_{in} is zero. For such an orientation, the order parameter S of the polymer chain is in the range $-0.5<S<0$. Thus, in order to obtain positive Δn_{th} for amorphous polymeric overlayer on the polymeric substrate, polymers with negative Δn_{int} can be used. Examples of such a polymers would include materials that have non-visible chromophores off of the polymer backbone. Such non-visible chromophores would include: vinyl, carbonyl, amide, imide, ester, carbonate, sulfone, azo, and aromatic heterocyclic and carbocyclic groups (e.g.. phenyl, naphthyl, biphenyl, terphenyl, phenol, bisphenol A, and thiophene). In addition, combinations of these non-visible chromophores could be desirable (i.e. copolymers). Examples of such polymers and their structures are shown below.

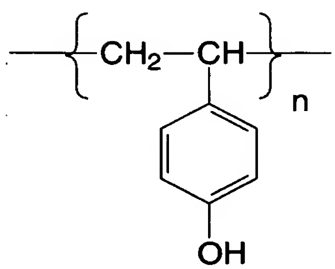
Example I:

poly (4 vinylbiphenyl)



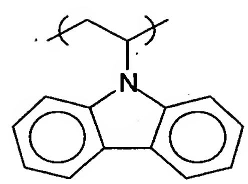
Example II:

poly (4 vinylphenol)



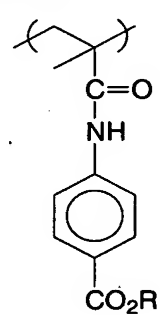
Example III:

poly (N-vinylcarbazole)



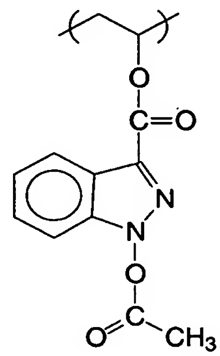
Example IV:

poly(methylcarboxyphenylmethacrylamide)



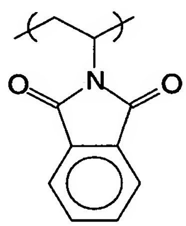
Example V:

poly[(1-acetylindazol-3-ylcarbonyloxy)ethylene]



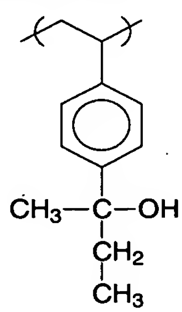
Example VI:

poly(phthalimidoethylene)



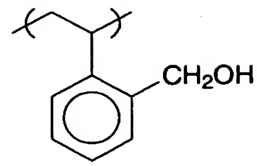
Example VII:

poly(4-(1-hydroxy-1-methylpropyl)styrene)



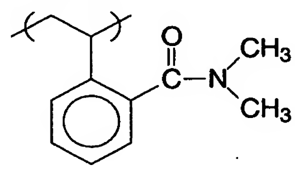
Example VIII:

poly(2-hydroxymethylstyrene)



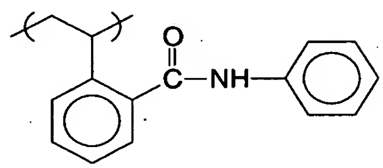
Example IX:

poly(2-dimethylaminocarbonylstyrene)



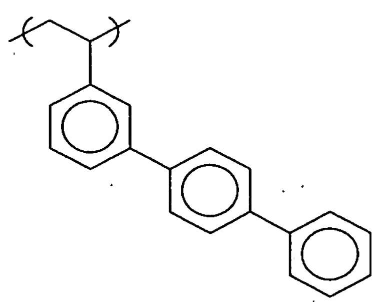
Example X:

poly(2-phenylaminocarbonylstyrene)



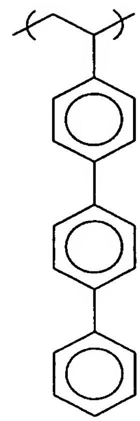
Example XI:

poly(3-(4-biphenylyl)styrene)



Example XII:

poly(4-(4-biphenylyl)styrene)



Another important factor is to obtain finite negative value of S. One way to achieve such negative S values is to solvent coat polymers whose glass transition temperature Tg is greater than 160°C. Such polymers will not have sufficient time to relax upon solvent evaporation and will retain a negative S value.

Examples of polymeric substrate can be made of polycarbonate, TAC, cyclic polyolephin, and other commonly used polymers in opto-electronic device applications. The thickness of polymer substrate should be sufficient to maintain mechanical integrity and handling ease. It is preferably between 10μm to 5mm or more preferably between 30μm to 2mm.

FIG. 5A is the elevation schematic for an absorptive polarizer **501** with an optical multilayer **301**. The multilayer **301** has a structure such as the one shown in FIGS. 3A, 3B and 3C. Polarizing layer **505** is made of, for example, dye absorbed PVA film. The substrate **503** can be the optical multilayer, such as **301** or other single layer polymeric material. FIG. 5B is yet another example of polarizer **507**. In this case, polarizing layer **505** is contiguously disposed on the multilayer **301**. This is a typical structure of the reflective polarizer. As is well known to those who are skilled in the art, layer of cholesteric liquid crystal functions as reflective polarizing layer. Also, reflective polarizer based on

periodically placed metal thin wire such as the one disclosed in US 6,081,376 can be the polarizing layer **505**.

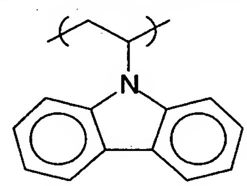
Elevation schematic of the optical-recoding medium **601** is shown in FIG.6. **603** is a recording layer. In magneto-optical recording media (MO), **603** is a magneto-optical layer made from, for example, rare-earth-cobalt-iron alloys. Optical multilayer **301** according to the invention is placed on the MO layer **603**. The light **607** to read the recorded signal is incident from multilayer **301** side. **605** is a protective layer.

The overlayer can easily be disposed on the polymeric substrate by and suitable method such as, for example, solvent casting.

The present invention is further illustrated by the following non-limiting examples of its practice.

Example:

Poly (N-vinylcarbazole) (polymer I) was obtained from Acros Organics and found to have a Tg of 161°C by differential scanning calorimetry (DSC).



Polymer I (15% solids in toluene) was spun cast onto a TAC substrate. R_{in} and R_{th} of this sample (and the TAC control) were measured with an ellipsometer (model M2000V, J.A. Woollam Co.) at λ=550nm. Results are shown in TABLE I.

The layer of polymer I did not show any sign of a long-range order. Therefore the layer was determined to be comprised of an amorphous polymer. This optical multilayer has a R_{th} between +30 and −30nm at a λ between 400 and 700nm. R_{th} of TAC and multilayer are shown as functions of λ with dash **701** and solid **703** lines, respectively in FIG. 7.

TABLE I

Polymer I Layer thickness (μm)	R_{in}, In-Plane Retardation (nm)	R_{th}, Out-of-Plane Retardation (nm)
0 (control)	3	-63
3	3	-7

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the scope of the invention. The entire contents of the patents and other publications referred to in this specification are incorporated herein by reference.

PARTS LIST

101	film
103	plane of the film
201	backlight assembly
203	backlight
205	diffusing film
207	brightness enhancement film
209	reflective polarizer
211	substrate
213	polarizing layer
215	absorptive polarizer
217	bottom substrate
219	absorptive polarizing layer
221	top substrate
301	optical multilayer
303	polymeric substrate
305	amorphous polymeric overlayer
401	liquid crystal
403	randomly oriented polymer chain in x-y plane
501	absorptive polarizer
503	substrate
505	polarizing layer
507	polarizer
601	optical recording medium
603	recording layer
605	protective layer
607	incident light for reading signal
701	dash line showing the wavelength dependence of R_{th} of TAC
703	solid line showing the wavelength dependence of R_{th} of the optical multilayer
S	order parameter

θ	an angle between the reference direction and the individual segment of the polymer chain
φ	angle of incidence of light
nx	index of refraction in x direction
ny	index of refraction in y direction
nz	index of refraction in z direction
no	ordinary index of refraction
ne	extraordinary index of refraction
Δn_{th}	out-of –plane birefringence
Δn_{in}	in-plane birefringence
Δn_{int}	intrinsic birefringence of polymer
Δn_p	birefringence of polymer
d	thickness of the film
R_{th}	out-of-plane phase retardation
R_{in}	in-plane phase retardation
λ	wavelength
I_{out}	out coming light intensity
I_{in}	input light intensity